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(19)

(54) PRODUCTION OF MIXTURES OF A CYCLOALKANOL AND A CYCLOALKANONE

(71) We, BADISCHE ANILIN- & SODA - FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The present invention relates to the production of cycloalkanol-cycloalkanone mixtures by oxidation of a cycloparaffin with oxygen and more particularly to an improved method of decomposing the intermediately formed hydroperoxide.

UK Patent 716,820 discloses the addition of a cobalt salt, which may be soluble in hydrocarbons, to mixtures such as are obtained in the oxidation of cyclohexane with air, after the oxidation in an acid medium.

We have now found that a mixture of a cycloalkanol and a cycloalkanone can be prepared in an advantageous manner by oxidation of a cycloparaffin of five to twelve carbon atoms in the liquid phase at a pressure of from 5 to 25 atmospheres gauge with a gas containing molecular oxygen, in the presence or absence of a heavy metal catalyst, and addition of a heavy metal salt catalyst which decomposes hydroperoxides to the reaction mixture after the oxidation is over, if the oxidation mixture is treated simultaneously with, or after, the addition of the heavy metal salt catalyst which decomposes hydroperoxides, with an aqueous solution of an alkali metal hydroxide or carbonate, the pH of the aqueous phase in the reaction mixture being kept at from 8 to 13, preferably at from 9 to 11, measured at 25°C.

The reaction conditions suitable for the oxidation of a cycloparaffin are known. Cycloparaffins of five to twelve carbon atoms may be oxidized; for example cyclopentane, cyclohexane, cyclooctane, cyclododecane or methylcyclohexane. The oxidation of cyclohexane has the greatest significance industrially.

The oxidation may be effected by passing air or other gas containing molecular oxygen through the cycloparaffin in the absence or presence of a conventional oxidation catalyst, i.e. a heavy metal catalyst of the transition metals. A reaction temperature of 130° to 190°C is generally maintained and a pressure of from 5 to 25 atmospheres gauge used. Generally the lower hydrocarbons can be better oxidized at the lower temperatures and the higher hydrocarbons at the higher temperatures.

In other respects the rules followed in the use of catalysts and/or initiators (for example isobutyraldehyde) apply for the most favorable temperature.

Instead of air (i.e. a gas mixture having about 20% by weight of oxygen and inert gases), other mixtures of gas with molecular oxygen may be used, for example mixtures of oxygen and carbon dioxide or mixtures of fresh air with the offgas from the reactor, i.e. mixtures of oxygen and nitrogen having a lower oxygen concentration than that of air, which contain for example only 10% of oxygen, or mixtures enriched with oxygen which contain for example 30% by weight of oxygen. When catalysts are used (primary catalysts) use may be made of conventional oxidation catalysts or those described in prior applications, particularly cobalt compounds, but also mixtures of cobalt compounds with manganese compounds or manganese compounds alone, or compounds of copper, iron, lead and/or nickel.

Compounds such as hexanates or naphthenates which are soluble in the cycloparaffin are generally used. It is however advantageous to use heavy metal compounds which are not precipitated by the water formed during the reaction, for example complex compounds of cobalt such as salicylaldehyde-

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diamine complexes (salcomines). Cobalt compounds which (a) are soluble in cycloparaffins and (b) are derived from strong acids are particularly suitable; "strong acids" include those whose activity is similar to that of phosphoric acid or sulfuric acid. Anions of monoalkyl esters of phosphoric acid, dialkyl esters of phosphoric acid, monoalkyl esters of sulfuric acid, alkylsulfonic acids, alkylphosphonic acids and dialkylphosphinic acids are therefore used in particular. The corresponding aralkyl compounds may be used instead of the alkyl compounds. To take advantage of the solubility of the compounds it is advantageous to use as anions those strong acids whose anions contain a long chain substituent, i.e. a substituent making them soluble in cycloparaffins. Alkyl compounds and esters which contain an alkyl radical of eight to twenty carbon atoms are therefore particularly suitable. Examples of such anions are therefore those of monooctyl phosphate, monododecyl phosphate, monolauryl phosphate, dioctyl phosphate, didodecyl phosphate, dilauryl phosphate, monooctyl sulfate, monododecyl sulfate, monolauryl sulfate, octylsulfonic acid, dodecylsulfonic acid, laurylsulfonic acid, octylphosphonic acid, dioctylphosphinic acid, dodecylphosphonic acid and didodecylphosphinic acid. Examples of araliphatic derivatives are the anions of octylbenzenesulfonic acid and of dodecylbenzenesulfonic acid. Since the oxidation may also be carried out in principle without catalysts, small additions of catalysts are effective. Generally from about 0.1 to 10 ppm, particularly from 0.2 to 0.5 ppm by weight of metal based on the cycloparaffin injected into the reactor is used.

The catalysts referred to in detail above are given only as examples; naturally all other catalysts conventionally used for such oxidation reactions may also be used. The oxidation may also be carried out without a primary catalyst. It is then advantageous to use oxidation temperatures of from 150° to 190°C.

After the reaction has taken place (i.e. after the reaction mixture has left the oxidation reactor) there is added to the reaction mixture a heavy metal salt conventionally used as an oxidation catalyst, particularly a cobalt salt, suitably in an amount of from 0.1 to 10 ppm by weight (based on the reaction mixture leaving the reactor), as the catalyst which decomposes hydroperoxides (secondary catalyst). This secondary catalyst is allowed to act on the reaction mixture for some time, for example from twenty to two hundred minutes. Generally from twenty to eighty minutes is enough. The temperature is suitably kept at from 80° to 170°C during this treatment. If the temperature is fairly low it may be advantageous to provide longer treatment times. Generally it is preferred however to correlate the type of catalyst, the amount of catalyst and the temperature so that the desired effect takes place after an aftertreatment period of from twenty to fifty minutes. As a rule it may be said that low temperatures are associated with long residence times and high temperatures are associated with short residence times. All conventional oxidation catalysts such as are set out above as primary catalysts may be used as secondary catalysts. It is preferred however to use cobalt compounds. Salts which have only slight solubility in the reaction mixture may be used, for example cobalt sulfate, cobalt nitrate or cobalt acetate; in particular however heavy metal salts which are soluble in cycloparaffins, especially cobalt salts such as naphthenates or ethylhexanates. It is of particular advantage to use as the heavy metal salts in the secondary catalysts the complex cobalt compounds described under the primary catalysts which are not only soluble in the cycloparaffin but are also resistant to hydrolysis in the reaction mixture and for example are not precipitated by the amounts of water present in the reaction mixture, i.e. those derived from strong acids or from complexes of the salcomine type. Examples of such cobalt salts have already been given in the enumeration of primary catalysts above.

The oxidation, as in all prior art methods, may be carried out in one or more stages, with or without intermediate water washes. The aftertreatment may be carried out after each of the oxidation stages or only after the last one.

It is often customary to wash not only with water but also with caustic alkali solutions for the complete removal of carboxylic acids formed as byproducts and to decompose byproducts, for example esters formed. A treatment with caustic alkali solutions, just like the washing with water, may be carried out after each of the individual oxidation stages or only after the final reactor. Particularly high yields are achieved when, in accordance with the invention, the reaction mixture, simultaneously with the addition of the secondary catalyst or after the secondary catalyst has been added, is treated with an aqueous solution of an alkali metal hydroxide or carbonate, the pH of the aqueous phase of the reaction mixture being kept at from 8 to 13, preferably from 9 to 11, measured at 25°C. This is achieved in the simplest fashion by using an about 1 to 20%, in particular a 5 to 10%, solution of an alkali metal carbonate, particularly sodium or potassium carbonate. An aqueous solution of an alkali metal hydroxide may be used provided it is metered in so that the said pH is maintained during the washing phase. The mixing of the reaction mixture with the alkali metal carbonate solution or with the alkali metal

hydroxide solution may be effected for example countercurrent in a packed column or cocurrent in a stirred container, at high temperature also in a pump acting as a mixer. At least sufficient alkali metal hydroxide or carbonate solution is used to neutralize acids present in the reaction mixture (i.e. the aqueous and organic phases) or to convert them into water-soluble salts which are extracted as such in the aqueous phase.

It is advantageous and in the case of the stirred container or mixing pump necessary to separate the oil and water phases through a separator or a separating vessel. Some of the solution containing alkali metal salts of carboxylic acids may thence be returned to the alkaline aftertreatment by adding fresh sodium hydroxide solution until a pH of for example 13 is achieved.

It is a further advantage of the aftertreatment with alkali in the pH range from 8 to 13 that the residence time of the secondary catalyst can be greatly shortened, especially when alkali solution is added at the same time as the secondary catalyst, so that from 0.1 minute to 30, preferably from 3 to 10 minutes is sufficient.

After any treatment with aqueous alkaline solution, the aqueous phase is separated. It is often favorable after the aftertreatment and after the after-washing with an alkaline solution in the pH range from 8 to 13 and separation of the two-phase system to carry out another washing with dilute aqueous caustic alkali solution and if necessary to wash the same until neutral.

The following Examples illustrate the invention.

EXAMPLE 1.

Oxidation of cyclohexane is carried out under the following conditions: air is passed under a pressure of 20 atmospheres gauge through cyclohexane which is kept at a temperature of 145°C in such an amount that a conversion of 5.3% is achieved. 0.7 ppm by weight of cobalt in the form of ethyl hexanate (based on cyclohexane) is added to the cyclohexane. The residence time of the cyclohexane in the oxidation zone is twenty-seven minutes. The reaction mixture obtained is washed twice with 2% by weight of water. The organic phase is then oxidized again with air at a temperature of 145°C and at a pressure of 20 atmospheres gauge for the same residence time of twenty-seven minutes. The reaction solution then obtained has 0.7 ppm by weight of cobalt in the form of the MDIT phosphate added to it. MDIT phosphate is the stoichiometric 1:1 mixture of the monoester and diester of o-phosphoric acid with isotridecanol. This secondary catalyst is allowed to act for a period of forty minutes at a temperature of 135°C.

The reaction mixture obtained is then treated twice, each time with 2% by volume of water, then once with such an amount of 25% by weight caustic soda solution for six minutes that the pH of the aqueous phase in the reaction mixture is kept at 11, and finally washed again with 2% by weight of water.

The reaction mixture is then distilled. Cyclohexanol and cyclohexanone are obtained in a yield of 71.5% of theory.

EXAMPLE 2.

The procedure of Example 1 is followed but the primary catalyst is added in the form of MDIT phosphate. MDIT phosphoric acid is the stoichiometric 1:1 mixture of the monoester and diester of o-phosphoric acid with isotridecanol. The yield with an otherwise identical method is 72.9% of theory. If the treatment with the secondary catalyst is carried out at 145°C instead of at 135°C and a residence time of sixty minutes is used, the yield of cyclohexanol and cyclohexanone is 73.3% of theory.

EXAMPLE 3.

The method described in Example 1 is used but without using a primary catalyst. A yield of 71.8% of theory is then achieved, while without using a secondary catalyst a yield of only 68.4% of theory is achieved.

EXAMPLE 4.

The procedure of Example 1 is followed but the reaction mixture is mixed immediately after the addition of the secondary catalyst with 0.3 part of a 10% sodium carbonate solution per part of reaction mixture and this mixture is left for a period of seven minutes at 135°C with constant stirring. The organic phase is then separated from the aqueous phase. The organic phase is washed again with water. The yield of cyclohexanone and cyclohexanol is 73.7% of theory.

EXAMPLE 5.

The procedure of Example 4 is followed but a primary catalyst is not used. The yield is then 73.2% of theory of cyclohexanone and cyclohexanol.

EXAMPLE 6.

The procedure of Example 2 is followed but the alkali treatment is modified. The Yields given in the following Table are achieved. The following abbreviations are used in the Table. Sec Cat=secondary catalyst 0.7 ppm of Co as:

MDITP=MDIT phosphate
EHSAC=ethylhexylamine - salicylaldehyde complex

K_2CO_3 = 10% by weight K_2CO_3 in excess (pH at 25°C: 10.0)
Na_2CO_3 = 10% by weight Na_2CO_3 in excess (pH at 25°C: 10.1)
NaOH = neutralization with aqueous solution which is kept at pH 11 with 25% NaOH
Percentages given are percentages of theory.

Modified alkali treatment

Sec Cat	K_2CO_3	Na_2CO_3	NaOH
MDITP	75.9%	77.4%	76.8%
EHSAC	76.2%	77.8%	77.0%
—	75.0%	76.9%	76.3%

In the following Table further results are set out under reaction conditions as in Example 1 with different primary catalysts (column 1), different secondary catalysts (columns 2 and 3) and different alkali treatments (column 4). Following oxidation in the presence of the primary catalyst there is a washing with water followed by addition of the secondary catalyst and alkali, then another water wash and a fractional distillation. Column 5 gives the results without a secondary catalyst, i.e. with only an alkali wash. Column 1 gives the primary catalyst consisting of 0.7 ppm by weight of cobalt in the form of
(A) ethyl hexanate
(B) MDIT phosphate
(C) dodecylbenzenesulfonate
Column 2 gives as secondary catalyst 0.7 ppm by weight of cobalt MDIT phosphate.
Column 3 gives as secondary catalyst 0.7 ppm by weight of cobalt ethylhexanate-salicylaldehyde diamine complex.
Column 4 gives the alkali used and
Column 5 gives the results without secondary catalyst.

1	2	3	4	5
A	71.2 71.9 72.3	71.2 72.0 72.2	25% NaOH 10% K_2CO_3 10% Na_2CO_3	70.7 71.5 71.8
B	73.1 75.9 77.4	73.4 76.6 77.8	25% NaOH 10% K_2CO_3 10% Na_2CO_3	72.9 75.0 76.9
C	73.1 75.8 77.6	73.5 76.4 78.0	25% NaOH 10% K_2CO_3 10% Na_2CO_3	72.4 75.0 76.4

WHAT WE CLAIM IS:—

1. A process for the production of a mixture of a cycloalkanol and a cycloalkanone by oxidation of a cycloparaffin of five to twelve carbon atoms in the liquid phase at a pressure of from 5 to 25 atmospheres gauge with a gas containing molecular oxygen in the presence or absence of a heavy metal catalyst, and addition to the reaction mixture after oxidation has taken place of a heavy metal salt catalyst which decomposes hydroperoxides, wherein an aqueous solution of an alkali metal hydroxide or carbonate is added to the oxidation mixture at the same time as, or subsequently to, the addition of the heavy metal salt catalyst which decomposes hydroperoxides, the pH of the aqueous phase in the reaction mixture being kept at from 8 to 13, measured at 25°C.

2. A process as claimed in claim 1 wherein the said pH of the reaction mixture is kept at from 9 to 11, measured at 25°C.

3. A process as claimed in claim 1 or 2 wherein the cycloparaffin used is cyclohexane.

4. A process as claimed in any of claims 1 to 3 wherein the oxidation of the cycloparaffin is carried out at a temperature of from 130 to 190°C.

5. A process as claimed in any of claims 1 to 4 wherein the oxidation is carried out at a temperature of from 150 to 190°C in the absence of any heavy metal catalyst.

6. A process as claimed in any of claims 1 to 5 wherein the heavy metal salt catalyst added to decompose hydroperoxides is a cobalt salt soluble in the cycloparaffin.

7. A process as claimed in any of claims 1 to 6 wherein the heavy metal salt catalyst added to decompose hydroperoxides is added in an amount from 0.1 to 10 ppm by weight, based on the weight of the oxidation mixture.

8. A process as claimed in any of claims 1 to 7 wherein the treatment of the oxidation mixture with the heavy metal salt catalyst to decompose hydroperoxides is carried out at a temperature of from 80 to 170°C.

9. A process as claimed in any of claims 1 to 8 wherein a 1 to 20% by weight solution of sodium or potassium carbonate is added to the oxidation mixture simultaneously with or subsequent to the addition of heavy metal salt catalyst.

10. A process as claimed in any of claims 1 to 9 wherein the organic phase of the mixture after treatment with the heavy metal salt catalyst and alkali metal carbonate or hydroxide is separated from the aqueous phase and washed with water or dilute aqueous caustic alkali.

11. A process as claimed in claim 1 carried out substantially as described in any of the foregoing Examples.

12. Cycloalkanols and cycloalkanones when obtained by the process claimed in any of claims 1 to 11.

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